PAUL SCHERRER INSTITUT

ELECTROCHEMISTRY LABORATORY

BATTERIES

Dynamics of the porous carbonaceous O_2 electrode interface : a combined XPS and OEMS study

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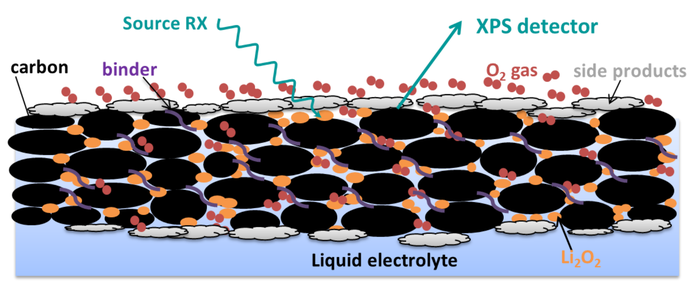
Motivation

- **Li-O_2 batteries**: complex interface at the porous electrode (gaseous, liquid and solid products)
  → **Complementary characterization techniques required**
- **X-Ray Photoelectron Spectroscopy** (XPS): most suitable technique to analyze the chemical composition of the extreme surface of materials (analysis depth ~ 5-10 nm)
- **Online Electrochemical Mass Spectrometry** (OEMS): O_2 and CO_2 gas detection



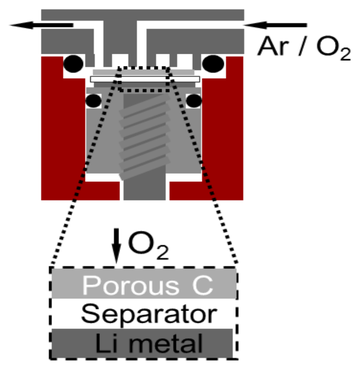
Experimental setup

Electrochemical measurements:

- **Porous electrode:** (thickness 200 µm): 85 wt % carbon (Imerys) / 15 wt % PTFE
- **Electrolyte:** 0.2 M LiTFSI in diglyme
- **Current density:** 0.1 mA/cm^2

Sample preparation for XPS:

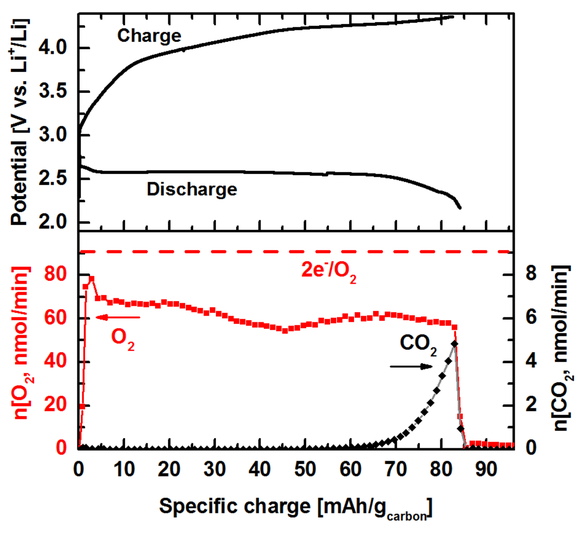
- Electrodes washed in diglyme
- Samples transferred using an air-tight transfer chamber



Scheme of the home-made Li-O_2 cell

Graphite SFG6

OEMS



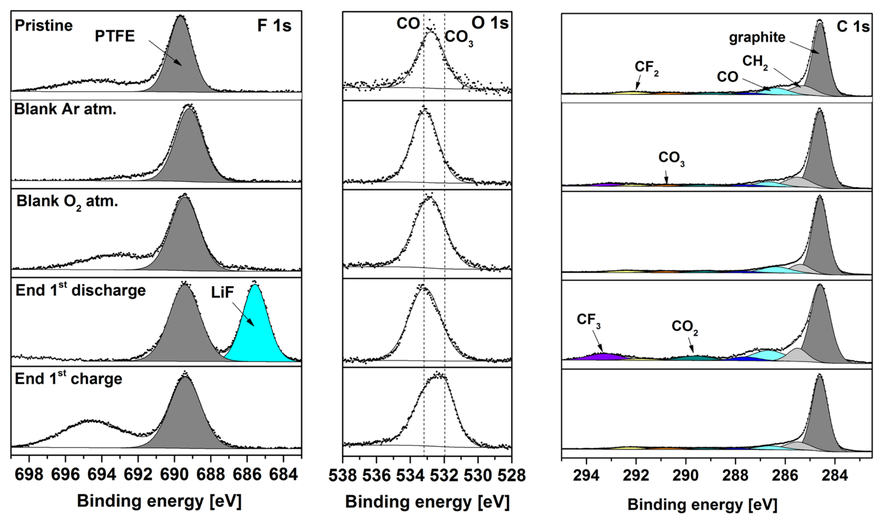
Discharge:

- low specific charge per mass of carbon
- **OEMS:** 2.06 e^- / O_2 for SFG6
- **XPS:**
  - thin interface (< 5-10 nm)
  - presence of LiF, CO_3 CO_2 and CO species
  - No evidence of Li_2O, Li_2O_2 or LiO_2
  - different interface layers on both sides

Charge:

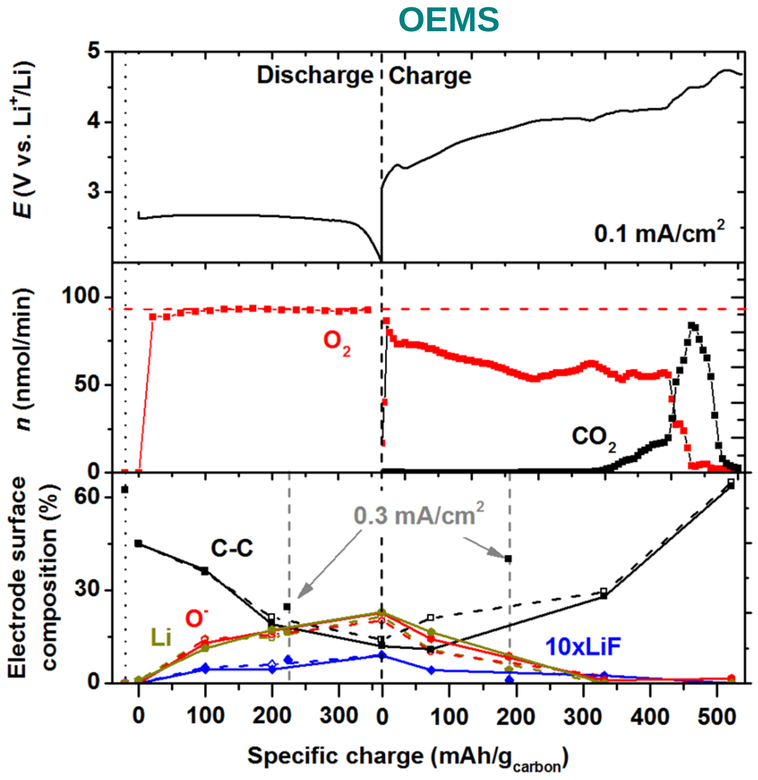
- **OEMS:**
  - O_2 gas
  - CO_2 evolution at the end of charge
- **XPS:** spectra similar to those of the pristine electrode → decomposition of the species formed during previous discharge (e.g. LiF)

XPS



Amorphous Carbon Super C65

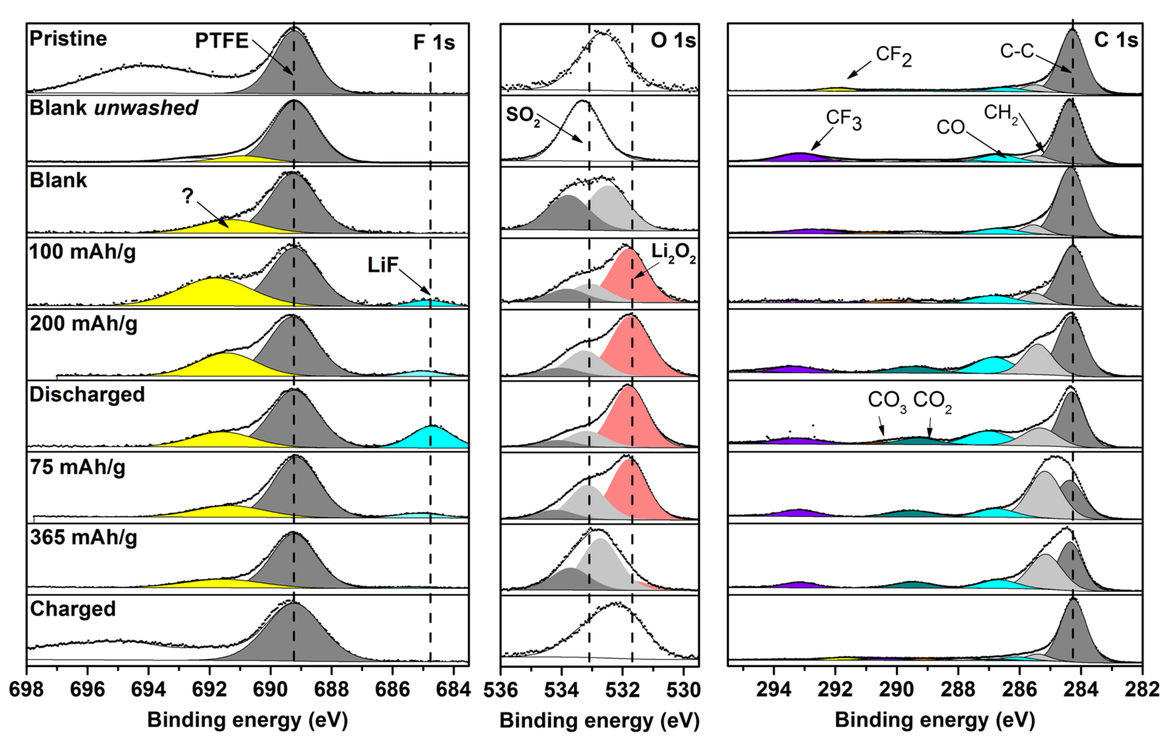
OEMS



Discharge: higher specific charge than SFG6
→ higher amount of Li_2O_2, more side-reactions?

- **OEMS:** 2.06 e^- / O_2 → Li_2O_2 formation
- **XPS:**
  - continuous formation of Li_2O_2 at the surface
  - thin interface (< 5-10 nm)
  - presence of LiF, CO_3 CO_2 and CO species → parasitic reactions
  - similar interface layers on both sides

XPS



Charge: higher specific charge than during discharge
→ parasitic reactions, shuttling?

- **OEMS:**
  - O_2 gas but less than expected
  - CO_2 evolution at the end of charge
- **XPS:** charge spectra similar to those of the pristine electrode → decomposition of the species formed during previous discharge

Conclusion

OEMS:
- **discharge:** ~ 2e^- / O_2 → formation of Li_2O_2
- **charge:** CO_2 evolution → parasitic reactions

XPS:
- **discharge:** detection of Li_2O_2 on O 1s spectrum and other side-products, interface thickness
- **charge:** decomposition of side-products formed during discharge

Carbon:
- Higher specific charge with Super C65 (higher specific surface area), higher amount of Li_2O_2
- Both carbons: side reactions during discharge and charge forming thin passivating layer

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